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(54) Title: ELECTROCHROMIC PANE ARRANGEMENT <div data-bbox="418 1108 1205 1516" data-label="Image"> </div> (57) Abstract <p>The invention relates to an electrochromic pane arrangement, comprising a first transparent electrode substrate (10), in particular a first glass pane, a second electrode substrate (12) arranged parallel to and at a distance from it, preferably a second glass pane, and an ion conducting layer (22) joining the two electrode substrates, which consists of a polymer matrix containing at least one salt including difficult to oxidise anions, at least one dopant suitable for the provision of cations, preferably metal ions, where the surface of a first electrode substrate facing towards the ion conducting layer is a first transparent electrode layer (14) and adjacent to it is an actively electrochromic layer (16) in surface contact with the ion conducting layer, preferably of tungsten trioxide, whose transparency and/or colour is reversibly variable as a result of absorption or emission of electrons via the first electrode layer and acceptance or emission of ions of the dopant from/to the ion conducting layer, and the surface of the second electrode substrate facing towards the ion conducting layer bears a second transparent electrode layer (18), and adjacent to it a transparent layer (20) in surface contact with the ion conducting layer and is suitable for the reversible storage of charge, preferably by ion insertion. The ion conducting layer includes at least one salt comprising a proportion of an easily oxidisable anion and/or at least one easily oxidisable organic compound, which is electrically neutral and undergoes no colour change upon changing the transmission of the electrochromic pane arrangement.</p>		

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Electrochromic Pane Arrangement

Specification

The invention relates to an electrochromic pane arrangement, comprising a first transparent electrode substrate, in particular a first glass pane, a second electrode substrate arranged parallel to and at a distance from, preferably a second glass pane, and an ion conducting layer joining the two electrode substrates which consists of a polymer matrix containing at least one salt including difficult to oxidise anions, at least one dopant suitable for the provision of cations, preferably metal ions, where the surface of a first electrode substrate facing towards the ion conducting layer is a first transparent electrode layer and adjacent to it is an actively electrochromic layer in surface contact with the ion conducting layer, preferably of tungsten trioxide, whose transparency and/or colour is reversibly variable as a result of absorption or emission of electrons via the first electrode layer and acceptance or emission of ions of the dopant from/to the ion conducting layer and the surface of the second electrode substrate facing towards the ion conducting layer bears a second transparent electrode layer, and adjacent to it a transparent layer in surface contact with the ion conducting layer and is suitable for the reversible storage of charge, preferably by ion insertion.

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An electrochromic laminated pane of this type is known from DE-A 41 16 059, where the two individual panes are joined to one another by means of a polyvinylbutyral layer which represents the ion conducting layer. The polyvinylbutyral layer, which is a film of polyvinylbutyral sufficiently well-known for the manufacture of laminated safety glass panes, contains LiClO_4 as dopant.

Electrochromic pane arrangements do not as a rule evidence any electrochromic properties in their freshly manufactured state, unless the electrochromic layer and/or the charge storage layer have been precharged by the insertion of positive ions. Otherwise, only after so-called preconditioning, does the pane arrangement acquire the property of variable light transmission. For the purpose of preconditioning, the pane arrangement is switched several times at low voltages and low cycle time after connection of a DC voltage. One cycle always consists of a colouration and bleaching period. During colouration and bleaching, identical or differing voltages can be applied, but with reversed polarities, where the pane incorporating the actively electrochromic layer, normally taking the form of a WO_3 layer, is connected during colouration as a cathode, but on the other hand as an anode during bleaching.

A first type of preconditioning is characterized by successive increase of the switching times and of the voltages applied.

It has been found favourable at the beginning of preconditioning to choose the colouration period of longer duration than the bleaching period, as then lower transmission values can be induced in the pane arrangement in stages. This method of preconditioning leads to a high transmission range, but is very time-consuming on account of the high number of cycles, this time requirement naturally increasing the cost

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of manufacture of the pane arrangement.

If it is desired to avoid the considerable time involved in the type of preconditioning used in the procedure described above, it is also known in the state of the art that the individual electrode layers can be charged with lithium ions. Either the actively electrochromic layer or the above-mentioned ion storage layer is charged with for example lithium ions before assembly to form the electrochromic pane arrangement. This is done by immersing the individual pane to be preconditioned in each case in a liquid electrolyte solution and applying a DC voltage. As counter electrode, there is a metal plate or also a glass pane matched to the pane size which is provided with an electronically conductive layer, where the electrolyte solution is composed as a rule of propylene carbonate and a lithium salt. By these means, it is possible to achieve a considerable reduction in the preconditioning time in comparison with the type of preconditioning described above, but there is the disadvantage that an additional operation is necessary, with the corresponding cleaning problems and difficulties involved in the production of the glass sandwich from the preconditioned individual panes, so that the production of electrochromic pane arrangements is relatively time-consuming, even with this second type of preconditioning.

An electrochromic pane arrangement of the type mentioned at the beginning is known from EP-B 0 083 988, where the ion conducting layer takes the form of a cast resin layer, where propylene carbonate is used as solvent for the conducting salt LiClO_4 . Here as well, the preconditioning problems described above occur.

In EP-B 0 098 416, an electrochromic pane arrangement similar to that of the generic type is described, where for the ion conducting layer a polymethyl methacrylate-based or a

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copolymer of methyl methacrylate/methacrylic acid-based lithium ion conductor is used. The preconditioning problems of the type described further above are also present with the procedure according to this publication.

Finally, an electrochromic pane arrangement of another type is known from EP-A 0 495 220, where no electrochromic layer is used, but a metal, for example Cu and/or Bi, is deposited on a glass surface, as a result of which darkening occurs. This reaction is reversible. On the counter-electrode not defined in detail, the anion of the salt in question is oxidized, this action also being reversible. To increase the solubility of CuCl and/or BiCl₃, a further salt can be added in the liquid electrolyte whose anions can form complexes with Cu. Lithium bromide is used in preference for this purpose. Finally, a salt with non-complexing anions can also be used, LiClO₄ being used in preference. According to the data of EP-B 0 495 220, the switching properties should be improved thereby. A problem with this procedure is the fact that in the event of a fracture of the pane arrangement or any other form of leak, the electrolyte liquid can escape, which will occasion considerable contamination problems. In addition, the use of the liquid electrolyte, in which lithium bromide and where applicable LiClO₄ are present for an increase in solubility or an improvement of the switching properties, does not permit the design of large-area switching elements. Finally, only relatively low operating voltages of not more than 2 volts are possible, as otherwise decomposition reactions can occur in the liquid electrolyte.

The purpose of the invention is to develop the pane arrangement of the generic type such that whilst retaining the advantages of the use of a solid electrolyte, which at the same time acts as a lamination between the two electrode substrates, particularly therefore glass panes, considerable simplification of the preconditioning and thus of the

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production as a whole becomes possible.

According to the invention, this problem is solved by the invention by the ion conducting layer including at least one salt comprising a proportion of an easily oxidisable anion and/or at least one easily oxidisable organic compound, which is electrically neutral and undergoes no colour change upon changing the transmission of the electrochromic pane arrangement. The said salt(s) comprising easily oxidisable anions is/are, therefore, partly or completely replaceable by said at least one easily oxidisable organic compound.

It has been found that such electrically neutral organic compounds which can be easily oxidised at the charge storage layer, connected as the anode, whereas WO_3 being the cathode, do not only provide electrons at the anode for accelerating the preconditioning phase. Furthermore, they can act as a plasticizer since they are not incorporated into the acrylate polymer.

Provision can be made for the salt(s) incorporating the difficult to oxidise and the easily oxidisable anion(s) to have different cations.

According to the invention, provision can also be made for the salt(s) incorporating the difficult to oxidise and the easily oxidisable anion(s) to have the same cation.

The invention is characterized by the use of lithium as cation for the difficult to oxidise salt(s).

The invention provides for the salt(s) with difficult to oxidise anions to consist of lithium cations with one variable anion and is/are selected from the group including perchlorate, tetrafluoroborate, hexafluorophosphate, hexafluoroarsenate and trifluoromethanesulphonate.

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The invention is characterized by the use of lithium, sodium, potassium, hydrogen, ammonium or tetraalkyl ammonium or mixtures of at least two of the aforementioned materials as cation(s) for the easily oxidisable salt(s).

According to the invention, provision can also be made for the salt(s) with easily oxidisable anions to be selected from the group including bromide, formate, cyanide, cyanate, acetate, trifluoroacetate, citrate, lactate, oxalate, benzoate, acetylacetonate, rhodanide, sulphite, thiosulphate, disulphite, dithionite, dithionate, phosphite and hypophosphite as well as mixtures of at least two of the aforementioned materials.

The invention also proposes that the proportion of the salt(s) in the ion conducting layer with difficult to oxidise anions should be 0.5 to 5.0 mol%.

Provision can be made thereby for the proportion of the salt(s) with difficult to oxidise anions to be 1 to 4 mol%.

The invention also provides for the proportion of the salt(s) with easily oxidisable anions to be 0.001 to 0.5 mol%.

Preferably, said easily oxidisable organic compound which is electrically neutral and undergoes no colour change upon changing the transmission of the electrochromic pane arrangement is selected from the group consisting of primary and/or secondary alcohols carrying at least one OH group and mixtures thereof.

One subgroup of such alcohols consists of primary and secondary aliphatic alcohols which are branched or unbranched and mixtures thereof. Examples are methanol, ethanol,

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1-propanol, 2-propanol, 1-butanol, 2-butanol, sec-butyl alcohol and higher homologues and mixtures thereof.

Another subgroup consists of branched or unbranched diols, triols and alcohols comprising more than three OH groups and mixtures thereof. Examples are ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, 1,4-butane diol, 2,3-butane diol, 1,5-pentane diol, 1,6-hexane diol, 1,2,3-propane triol, trimethylol propane, pentaerythritol or the like and mixtures thereof.

Still another subgroup consists of saturated cyclic primary and secondary alcohols and mixtures thereof. Examples are cyclopropanol, cyclobutanol, cyclopentanol, cyclohexanol, 1-cyclopropylethanol or the like and mixtures thereof.

Preferably, the proportion of primary and/or secondary alcohols carrying at least one OH group is 0.01 to 5 mol%.

Provision can also be made for the thickness of the ion conducting layer to be 0.2 to 2.0 mm.

The invention also provides for the thickness of the ion conducting layer to be approximately 1 mm.

The invention also proposes that the ion conducting layer should take the form of an acrylate based cast resin layer.

Provision can be made for the salts and/or the easily oxidisable organic compound(s) of the ion conducting layer being introduced into the cast resin mixture for manufacture of the polymer matrix for the ion conducting layer before polymerization.

According to the invention, provision can be made for the

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cast resin mixture for manufacture of the polymer matrix for the ion conducting layer incorporating at least one acrylic and/or methacrylic ester, at least one plasticizer also acting as solvent for the salts and at least one polymerization initiator.

The invention also proposes that the cast resin mixture incorporates at least one cross-linking agent.

Provision can be made thereby for the acrylic and or methacrylic ester(s) of the cast resin mixture for the manufacture of the polymer matrix of the ion conducting layer to include at least one component of the following group: all branched or unbranched saturated aliphatic (meth)acrylic esters, in particular methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl- and 2-ethyl-1-hexyl-(meth)acrylic esters.

Provision can also be made for the proportion of the cast resin mixture of saturated aliphatic (non-functionalised) (meth)acrylic esters to be between 60 and 95 mol%.

The invention also provides for the proportion of the cast resin mixture of saturated aliphatic (non-functionalised) (meth)acrylic esters is between 70 and 90 mol%.

Provision can be made thereby for the cast resin mixture to incorporate at least one hydroxyalkyl ester of acrylic or methacrylic acid which has at least one primary and/or secondary and/or tertiary hydroxy group which is to be found in a branched or unbranched alkyl group.

The invention also proposes that the hydroxyalkyl ester(s) be selected from the group containing 2-hydroxyethyl acrylate, 1-hydroxypropyl acrylate, 2-hydroxypropyl acrylate, 1,4-butanediol monoacrylate and 1,6-hexanediol monoacrylate.

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The invention also proposes that the proportion of the cast resin mixture of hydroxyalkyl (meth)acrylic ester(s) be 0.5 to 15 mol%.

Provision can also be made for the proportion of the cast resin mixture of hydroxyalkyl (meth)acrylic ester(s) to be 1 to 5 mol%.

Provision can also be made thereby for the plasticizer(s) to be selected from the group containing propylene carbonate, ethylene carbonate, gamma-butyrolactone, N-methyl pyrrolidone, 1,3-dimethyl-2-imidazolidinone, 3-methyl-2-oxazolidinone, dimethyl formamide, dimethyl sulphoxide, dimethoxy ethane and diethylene glycol monoethyl ether, as well as mixtures of at least two of the aforementioned materials.

The invention also provides for the proportion of the cast resin mixture of plasticizer(s) to be 5 to 30 mol%.

According to the invention, provision can also be made for the proportion of the cast resin mixture of plasticizer(s) is at the most 25 mol%.

Provision can also be made for the cross-linking agent(s) to incorporate at least a compound which possesses at least two acrylate or methacrylate groups per molecule, such as 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, ethylene glycol diacrylate, di-ethylene glycol diacrylate, tri-ethylene glycol diacrylate, propylene glycol diacrylate, di-propylene glycol diacrylate, tri-propylene glycol diacrylate, tri-methylol propane triacrylate, ditrimethylol propane tetraacrylate, dipentaerythritol pentaacrylate and/or pentaerythritol tetraacrylate.

The invention also provides for the proportion of the cast

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resin mixture of cross-linking agent is up to 10 mol%.

Furthermore, the invention provides for the proportion of the cast resin mixture of cross-linking agent to be 5 mol% at maximum.

Provision can also be made for the polymerization initiator proportion of the cast resin mixture is 0,01 to 0,5 mol%.

The invention also provides for the polymerization initiator proportion of the cast resin mixture to be 0.02 to 0.3 mol%.

Provision can also be made thereby for the polymerization initiator(s) to be selected from the group incorporating hydroxycyclohexyl-phenyl ketone, 2-hydroxy-2-methylphenyl-1-propanon, 2,4,6-trimethylbenzoyldiphenyl phosphine oxide and/or ethyl-2,4,6-trimethylbenzoylphenylphosphinate.

The invention also proposes that the thickness of the first and/or of the second electrode layer be 100 to 400 nm.

The invention also provides for the thickness of the first (14) and/or the second electrode layer (18) to be approximately 300 nm.

Provision can be made thereby for the first electrode layer and/or the second electrode layer to consist of indium tin oxide.

Provision can be made thereby for the first electrode layer and/or the second electrode layer to consist of fluorine-doped tin oxide.

Provision can be made thereby for the thickness of the actively electrochromic layer (16) to be 250 to 500 nm.

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The invention also provides for the thickness of the actively electrochromic layer to be approximately 350 nm.

Provision can also be made for the second electrode layer to bear on its side facing towards the ion conducting layer a passively or actively electrochromic charge storage layer.

The invention also proposes that the charge storage layer (20) have a thickness of 200 up to 400 nm.

Provision can also be made for the charge storage layer to have a thickness of 280 nm.

Finally, the invention also provides for the charge storage layer to consist of cerium titanium oxide, nickel oxide, cobalt oxide, chromium oxide, vanadium oxide and/or iridium oxide.

The mechanisms underlying the invention are the following:

If the polarity is chosen as to colour the electrochromic pane the lithium ions, usually present, dissolved in the ion conducting layer are attracted to the WO_3 cathode and intercalate into this layer. To maintain electron neutrality it is required that at that time either a respective number of cations from the counter electrode enter into the polymer or a respective number of anions migrate into the counter electrode. None of these events will occur with freshly manufactured panes, since there are, at the beginning, no cations present at the counter electrode, on the other hand, the rather large perchlorate ions are prevented from entering into the counter electrode.

The invention is based on the surprising principle that it is possible to achieve considerable simplification of the manufacture of electrochromic pane arrangements by

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eliminating the necessity for preconditioning by means of cyclic colouration and bleaching or individual preconditioning of the individual panes used in the immersion process by using for manufacture of the ion conducting layer a cast resin mixture to which small quantities of in particular lithium salts with easily oxidisable anions, in particular lithium bromide, and/or one or more easily oxidisable electrically neutral organic compounds, in particular diols and triols, are added.

With the example of the additive lithium bromide, the "autogenous preconditioning" according to the invention can be illustrated as follows:

If a voltage is applied to the pane arrangement according to the invention such that the electrochromic layer is polarized as cathode, lithium ions from the ion conducting layer can enter the tungsten oxide coating. The voltage source provides the electrons necessary for charge equalization. This operation leads to a change in the oxidation state of some of the tungsten ions of the tungsten-(VI)-oxide layer of + 6 to +5. The simultaneous presence of both tungsten ions causes a change in the absorption behaviour and consequently colouration. This process is of course only made possible by an oxidation reaction taking place on the second electrode layer, that is to say the counter-electrode, which can provide sufficient electrons. This oxidation reaction consists of the irreversible electron emission by the bromide ion. In addition, elemental bromine is produced which is intercepted by residual monomers which are always present in the cast resin. It is necessary for this oxidation reaction to be irreversible and only to take place in the initial stage of preconditioning. For this reason, the quantity of lithium bromide added must be kept low. According to the invention, one therefore uses between 0.01 and 0.5 mol% in the cast resin mixture.

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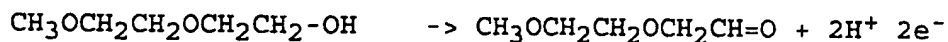
If the electrochromic pane arrangement is coloured in the manner described above, bleaching can be achieved by means of polarity reversal. When this happens, lithium removal takes place on the actively electrochromic layer, and at the same time the oxidation state of the tungsten resumes the value of + 6. The actively electrochromic layer lightens, where upon the reactions described above, that is to say lithium intercalation and lithium emission, are reversible processes. At the same time, with lithium emission of the actively electrochromic layer, that is to say of the tungsten oxide electrode, lithium intercalation in the cerium titanium oxide counter-electrode used preferably according to the invention is initiated, which is also reversible here. The irreversible oxidation reaction of the bromide ions now has no further significance for the function of the electrochromic pane arrangement after the process of "autogenous preconditioning" described above has been completed.

As a representative for electrically neutral easily oxidisable organic compounds which are suitable for the invention, diethylene glycol monomethylether is chosen.

Whereas,



it is



in the case of the electrically neutral easily oxidisable organic compounds, and the process will run similarly as described above with respect to lithium bromide.

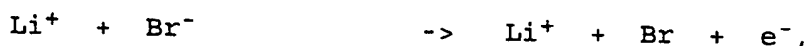
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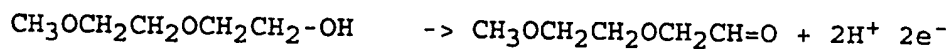
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the art of technology, the function of the electrode layers, preferably indium tin oxide coatings, consists of rendering the surface of the glass panes used preferably as transparent electrode substrate electrically conductive. This is also necessary on the first electrode substrate as the actual electrochromic material, in the case of WO_3 is an insulator. The use of the $\text{Ce}_x\text{Ti}_y\text{O}_z$ -coated counter-electrode has in contrast to the use of a pure ITO (indium tin oxide) counter-electrode the advantage that irreversible brown discolouration takes place to a negligible extent or not at all. In addition, the $\text{Ce}_x\text{Ti}_y\text{O}_z$ coating acts as an ion storage medium.

The function of the cast resin, whose principal component is a mixture of various acrylic and/or methacrylic esters, consists in the case of the pane according to the invention of establishing a conductive connection between the two electrode layers. For this purpose, the cast resin is ion conductive, for which lithium salts have proved particularly suitable. The function of the plasticizer is assumed preferably by propylene carbonate (4-methyl-1,3-dioxolane-2-on), a polar aprotic solvent which possesses a low melting point (-48°C) and a high boiling point (241°C). These properties are particularly favourable for high and low temperature stability of the finished electrochromic pane arrangement according to the invention. To the acrylate is added preferably approximately 0.1 mol% polymerization initiator, as well as if necessary a cross-linking agent.

Further features and advantages of the invention are stated in the description below, in which an embodiment is explained in detail with the aid of the schematic drawing.

Here, the drawing consisting of a single Figure shows an embodiment of an electrochromic pane arrangement in section perpendicular to the plane of the electrode substrates.

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As the drawing shows, the electrochromic pane arrangement according to the invention incorporates in the case of the embodiment shown here a first glass pane 10 and a second glass pane 12, both of which are essentially flat and measure approximately 40 x 80 cm². The first glass pane 10 bears on its surface facing downwards in the drawing a first electrode layer 14 which is an indium tin oxide (ITO) layer with a thickness of approximately 300 nm. To the first electrode layer 14 is applied an actively electrochromic layer 16 of WO₃ with a thickness of 350 nm.

The second glass pane 12 bears on its side facing towards the first glass pane 10 a second electrode layer 18, also consisting of indium tin oxide, with a thickness of 300 nm. Adjacent to the second electrode layer 18 on the side opposite the second glass pane 12 is an charge storage layer or ion storage layer 20 of Ce_xTi_yO_z having a thickness of 280 nm. The two glass panes 10, 12 provided with the coatings described above are joined to one another in the fashion of a laminated pane by an ion conducting layer 22, which in the case of the embodiment shown has a thickness of 1 mm and consists of a polymer matrix with dissolved salts.

Contacts are provided at the first 14 and second 18 electrode layer, as exemplarily shown at reference numeral 26 for the second electrode layer 18, to be connected with a suitable power supply. A fluid-tight sealing 24 is designed to enclose the ion conducting layer 22 and to accommodate, at least partly, the contacts, as 26.

In the case of the embodiment shown, the cast resin mixture which has been used for manufacture of the ion conducting layer 22 has a composition of 76.6 mol% n-butylacrylic ester, 1.9 mol% 1,4-butanediol monoacrylate, 17.9 mol% propylene carbonate, 3.1 mol% LiClO₄ and 0.5 mol% LiBr. Good results

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have also been achieved with a cast resin mixture which incorporated 60 - 90 mol% n-butyl acrylic ester, 1.5 - 2 mol% butanediol monoacrylate, 10 - 20 mol% propylene carbonate, 1 - 5 mol% LiClO_4 and 0.01 - 1 mol% LiBr.

Of course, the plasticizer component propylene carbonate can also be replaced by other plasticizers. In the same way, lithium bromide (LiBr) is only a representative of the class of substances of lithium salts with easily oxidisable anions, so that here as well other changes are possible.

As polymerization initiators for the curing of the cast resin mixture initiated by UV light, suitable are in particular hydroxycyclohexyl phenyl ketone, obtainable under the trade name Irgacure 184, 2-hydroxy-2-methylphenyl-1-propanon, obtainable under the trade name Irgacure 1173, a mixture of 70 % Irgacure 1173 and 30 % Lucirin TPO, available under the trade name Darocure 4263, a mixture of 50 % Irgacure 1173 and 50 % Lucirin TPO, available under the trade name Darocure 4265, 2,4,6-trimethylbenzoyl diphenylphosphine oxide, available under the trade name Lucirin TPO and/or ethyl-2,4,6-trimethylbenzoylphenylphosphinate.

Especially preferred are the above mentioned catalysts Darocure 4263 or Irgacure 184.

Below are given embodiments of the cast resin mixture usable according to the invention in addition to all other components for the ion conducting layer:

Example 1

983 g corresponding to 78.55 weight% or 76.21 mol% n-butyl acrylate, 24 g corresponding to 1.92 weight% or 1.66 mol% 1,4-butanediol monoacrylate, 185 g corresponding to 14.78 weight% or 17.99 mol% propylene carbonate, 33 g corresponding

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to 2.64 weight% or 3.08 mol% lithium perchlorate, 1.2 g corresponding to 0.10 weight% or 0.14 mol% lithium bromide, 24 g corresponding to 1.92 weight% or 0.86 mol% tripropylene glycol diacrylate and 1.3 g corresponding to 0.10 weight% or 0.06 mol% polymerization initiator (Darocure 4263).

Example 2

950 g corresponding to 73.73 weight% or 71.88 mol% n-butyl acrylate, 50 g corresponding to 3.88 weight% or 3.78 mol% tert-butyl acrylate, 32 g corresponding to 2.48 weight% or 2.15 mol% 1,4-butanediol monoacrylate, 150 g corresponding to 11.64 weight% or 14.24 mol% propylene carbonate, 30 g corresponding to 2.33 weight% or 3.30 mol% ethylene carbonate, 33 g corresponding to 2.56 weight% or 3.00 mol% lithium perchlorate, 1.5 g corresponding to 0.12 weight% or 0.17 mol% lithium bromide, 40 g corresponding to 3.10 weight% or 1.40 mol% tripropylene glycol diacrylate and 2.0 g corresponding to 0.2 weight% or 0.07 mol% polymerization initiator (Darocure 4265).

In the following examples, lithium bromide has been replaced partially (example 3) or completely (example 4) by alcohols suitable for the invention.

Example 3

950 g corresponding to 72.55 weight% or 70.60 mol% n-butyl acrylate, 50 g, corresponding to 3.82 weight% or 3.27 mol% tert-butylacrylate, 40 g corresponding to 3.05 weight% or 2.64 mol% 1,4-butanediol monoacrylate, 160 g corresponding to 12.22 weight% or 14.92 mol% propylene carbonate, 30 g corresponding to 2.29 weight% or 3.24 mol% ethylene carbonate, 35 g corresponding to 2.67 weight% or 3.12 mol% lithium perchlorate, 1 g corresponding to 0.08 weight% or 0.11 mol% lithium bromide, 40 g corresponding to 3.05

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weight% or 1.38 mol% tripropylene glycol diacrylate, 2 g corresponding to 0.15 weight% or 0.23 mol% 1,2,3-propane triol and 1.5 g corresponding to 0.11 weight% or 0.04 mol% polymerization initiator, namely 2,4,6-trimethylbenzoyl diphenyl phosphine oxide, acting as UV initiator.

Example 4

235 g corresponding to 77.48 weight% or 74.50 mol% n-butyl acrylate, 10 g corresponding to 3.30 weight% or 2.82 mol% 1,4-butanediol monoacrylate, 45 g corresponding to 14.84 weight% or 17.91 mol% propylene carbonate, 3 g corresponding to 1.00 weight% or 0.92 mol% trimethylol propane, 10 g corresponding to 3.30 weight% or 3.81 mol% lithium perchlorate, and 0.3 g corresponding to 0.10 weight% or 0.04 mol% polymerization initiator, namely 2,4,6-trimethylbenzoyl diphenyl phosphine oxide, acting as UV initiator.

The manufacture of the pane arrangement described above took place in a manner such that first of all the cast resin mixture with all components was produced, that is to say including the lithium salts and/or the easily oxidisable organic compound. Then, a laminated pane was produced by casting in the manner known from the manufacture of laminated safety panes, which then represented the electrochromic arrangement according to the invention.

By means "autogenous preconditioning", in the manner already described above, satisfactory function of the pane arrangement was achieved without tedious preconditioning cycles.

The features of the invention disclosed in the preceding description, in the drawing, as well as in the claims can be essential both individually as well as in any combination for realization of the invention in its various embodiments.

REFERENCE NUMERAL LIST

- 10 first glass pane
- 12 second glass pane
- 14 first electrode layer
- 16 actively electrochromic layer
- 18 second electrode layer
- 20 charge storage layer
- 22 ion conducting layer
- 24 sealing
- 26 contact

Patent Claims

1. Electrochromic pane arrangement, comprising a first transparent electrode substrate, in particular a first glass pane, a second electrode substrate arranged parallel to and at a distance from it, preferably a second glass pane, and an ion conducting layer joining the two electrode substrates, which consists of a polymer matrix containing at least one salt including difficult to oxidise anions, at least one dopant suitable for the provision of cations, preferably metal ions, where the surface of a first electrode substrate facing towards the ion conducting layer is a first transparent electrode layer and adjacent to it is an actively electrochromic layer in surface contact with the ion conducting layer, preferably of tungsten trioxide, whose transparency and/or colour is reversibly variable as a result of absorption or emission of electrons via the first electrode layer and acceptance or emission of ions of the dopant from/to the ion conducting layer, and the surface of the second electrode substrate facing towards the ion conducting layer bears a second transparent electrode layer, and adjacent to it a transparent layer in surface contact with the ion conducting layer and is suitable for the reversible storage of charge, preferably by ion insertion,

characterized in that the ion conducting layer (22) includes

at least one salt comprising a proportion of an easily oxidisable anion

and/or

at least one easily oxidisable organic compound, which is electrically neutral and undergoes no colour change upon changing the transmission of the electrochromic pane arrangement.

2. Pane arrangement in accordance with claim 1, characterized in that the salt(s) incorporating the difficult to oxidise and the easily oxidisable anion(s) has/have different cations.

3. Pane arrangement in accordance with claim 1, characterized in that the salt(s) incorporating the difficult to oxidise and the easily oxidisable anion(s) has/have the same cation.

4. Pane arrangement in accordance with one of the preceding claims, characterized by the use of lithium as cation for the difficult to oxidise salt(s).

5. Pane arrangement in accordance with claim 4, characterized in that the salt(s) with difficult to oxidise anions consist(s) of lithium cations with one variable anion and is/are selected from the group including perchlorate, tetrafluoroborate, hexafluorophosphate, hexafluoroarsenate and trifluoromethanesulphonate.

6. Pane arrangement in accordance with one of the preceding claims, characterized by the use of lithium, sodium, potassium, hydrogen, ammonium or tetraalkyl ammonium or mixtures of at least two of the aforementioned materials as cation(s) for the easily oxidisable salt(s).

7. Pane arrangement in accordance with one of the preceding claims, characterized in that the salt(s) with easily oxidisable anions is/are selected from the group including

bromide, formiate, cyanide, cyanate, acetate, trifluoroacetate, citrate, lactate, oxalate, benzoate, acetylacetonate, rhodanide, sulphite, thiosulphate, disulphite, dithionite, dithionate, phosphite and hypophosphite, as well as mixtures of at least two of the aforementioned materials.

8. Pane arrangement in accordance with one of the preceding claims, characterized in that the proportion of the salt(s) in the ion conducting layer with difficult to oxidise anions is 0.5 to 5.0 mol%.

9. Pane arrangement in accordance with claim 8, characterized in that the proportion of the salt(s) with difficult to oxidise anions is 1 to 4 mol%.

10. Pane arrangement in accordance with one of the preceding claims, characterized in that the proportion of the salt(s) with easily oxidisable anions is 0.001 to 0.5 mol%.

11. Pane arrangement in accordance with claim 1, characterized in that said easily oxidisable organic compound which is electrically neutral and undergoes no colour change upon changing the transmission of the electrochromic pane arrangement is selected from the group consisting of primary and/or secondary alcohols carrying at least one OH group and mixtures thereof.

12. Pane arrangement in accordance with claim 11, characterized in that said alcohol is selected from the group consisting of primary and secondary aliphatic alcohols which are branched or unbranched and mixtures thereof.

13. Pane arrangement in accordance with claim 12, characterized in that said aliphatic alcohol is selected from the group consisting of methanol, ethanol, 1-propanol, 2-propanol,

1-butanol, 2-butanol, sec-butyl alcohol, and higher homologues and mixtures thereof.

14. Pane arrangement in accordance with claim 11, characterized in that said alcohol is selected from the group consisting of branched or unbranched diols, triols and alcohols comprising more than three OH groups and mixtures thereof.

15. Pane arrangement in accordance with claim 14, characterized in that said alcohol is selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, 1,4-butane diol, 2,3-butane diol, 1,5-pentane diol, 1,6-hexane diol, 1,2,3-propane triol, trimethylol propane, pentaerythritol or the like and mixtures thereof.

16. Pane arrangement in accordance with claim 11, characterized in that said alcohol is selected from the group consisting of saturated cyclic primary and secondary alcohols and mixtures thereof.

17. Pane arrangement according to claim 16, characterized in that said alcohol is selected from the group consisting of cyclopropanol, cyclobutanol, cyclopentanol, cyclohexanol, 1-cyclopropylethanol or the like and mixtures thereof.

18. Pane arrangement according to one of claims 11 to 17, characterized in that the proportion of primary and/or secondary alcohols carrying at least one OH group is 0.01 to 5 mol%.

19. Pane arrangement in accordance with one of the preceding claims, characterized in that the thickness of the ion conducting layer (22) is 0.2 to 2.0 mm.

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20. Pane arrangement in accordance with claim 19, characterized in that the thickness of the ion conducting layer (22) is approximately 1 mm.

21. Pane arrangement in accordance with one of the preceding claims, characterized in that the ion conducting layer (22) takes the form of an acrylate based cast resin layer.

22. Pane arrangement in accordance with claim 21, characterized in that the salts and/or the easily oxidisable organic compound(s) of the ion conducting layer are introduced into said cast resin mixture for manufacture of the polymer matrix for the ion conducting layer (22) before polymerization.

23. Pane arrangement in accordance with claim 22, characterized in that the cast resin mixture for manufacture of the polymer matrix for the ion conducting layer (22) includes at least one acrylic and/or methacrylic ester, at least one plasticizer also acting as solvent for the salts and at least one polymerization initiator.

24. Pane arrangement in accordance with claim 23, characterized in that the cast resin mixture incorporates at least one cross-linking agent.

25. Pane arrangement in accordance with claim 23 or 24, characterized in that the acrylic and/or methacrylic ester(s) of the cast resin mixture for the manufacture of the polymer matrix of the ion conducting layer (22) include(s) at least one component of the following group: all branched or unbranched saturated aliphatic (meth)acrylic ester, in particular methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl- and 2-ethyl-1-hexyl-(meth)acrylic esters.

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26. Pane arrangement in accordance with one of claims 23 to 25, characterized in that the proportion of the cast resin mixture of saturated aliphatic (non-functionalised) (meth)acrylic esters is between 60 and 95 mol%.

27. Pane arrangement in accordance with claim 26, characterized in that the proportion of the cast resin mixture of saturated aliphatic (non-functionalised) (meth)acrylic esters is between 70 and 90 mol%.

28. Pane arrangement in accordance with one of claims 23 to 27, characterized in that the cast resin mixture incorporates at least one hydroxyalkyl ester of acrylic or methacrylic acid which has at least one primary and/or secondary and/or tertiary hydroxy group which is to be found in a branched or unbranched alkyl group.

29. Pane arrangement in accordance with claim 28, characterized in that the hydroxyalkyl ester(s) is/are selected from the group comprising 2-hydroxyethyl acrylate, 1-hydroxypropyl acrylate, 2-hydroxypropyl acrylate, 1,4-butanediol monoacrylate and 1,6-hexanediol monoacrylate.

30. Pane arrangement in accordance with claim 28 or 29, characterized in that the proportion of the cast resin mixture of hydroxyalkyl (meth)acrylic ester(s) is 0.5 to 15 mol%.

31. Pane arrangement in accordance with claim 30, characterized in that the proportion of the cast resin mixture of hydroxyalkyl (meth)acrylic ester(s) is 1 to 5 mol%.

32. Pane arrangement in accordance with one of claims 23 to 31, characterized in that the plasticizer(s) is/are selected from the group comprising propylene carbonate, ethylene carbonate, gamma-butyrolactone, N-methyl pyrrolidone, 1,3-dimethyl-2-imidazolidinone, 3-methyl-2-oxazolidinone, dimethyl

formamide, dimethyl sulphoxide, dimethoxy ethane and diethylene glycol monoethyl ether, as well as mixtures of at least two of the aforementioned materials.

33. Pane arrangement in accordance with one of claims 23 to 32, characterized in that the proportion of the cast resin mixture of plasticizer(s) is 5 to 30 mol%.

34. Pane arrangement in accordance with claim 33, characterized in that the proportion of the cast resin mixture of plasticizer(s) is at the most 25 mol%.

35. Pane arrangement in accordance with one of claims 24 to 34, characterized in that the cross-linking agent(s) includes at least a compound which possesses at least two acrylate or methacrylate groups per molecule, such as 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, ethylene glycol diacrylate, di-ethylene glycol diacrylate, tri-ethylene glycol diacrylate, propylene glycol diacrylate, di-propylene glycol diacrylate, tri-propylene glycol diacrylate, tri-methylol propane triacrylate, ditrimethylol propane tetraacrylate, dipentaerythritol pentaacrylate and/or pentaerythritol tetraacrylate.

36. Pane arrangement in accordance with one of claims 24 to 35, characterized in that the proportion of the cast resin mixture of cross-linking agent is up to 10 mol%.

37. Pane arrangement in accordance with claim 36, characterized in that the proportion of the cast resin mixture of cross-linking agent is of 5 mol% at maximum.

38. Pane arrangement in accordance with one of claims 24 to 37, characterized in that the polymerization initiator proportion of the cast resin mixture is 0.01 to 0.5 mol%.

39. Pane arrangement in accordance with claim 38, characterized in that the polymerization initiator proportion of the cast resin mixture is 0.02 to 0.3 mol%.

40. Pane arrangement in accordance with one of claims 24 to 39, characterized in that the polymerization initiator(s) is/are selected from the group comprising hydroxycyclohexyl-phenyl ketone, 2-hydroxy-2-methylphenyl-1-propanone, 2,4,6-trimethylbenzoyl-diphenyl phosphine oxide and/or ethyl-2,4,6-trimethylbenzoylphenylphosphinate.

41. Pane arrangement in accordance with one of the preceding claims, characterized in that the thickness of the first (14) and/or of the second electrode layer (18) is 100 to 400 nm.

42. Pane arrangement in accordance with claim 41, characterized in that the thickness of the first (14) and/or the second electrode layer (18) is approximately 300 nm.

43. Pane arrangement in accordance with one of the preceding claims, characterized in that the first electrode layer (14) and/or the second electrode layer (18) consist(s) of indium tin oxide.

44. Pane arrangement in accordance with one of claims 1 to 43, characterized in that the first electrode layer (14) and/or the second electrode layer (18) consist(s) of fluorine-doped tin oxide.

45. Pane arrangement in accordance with of the preceding claims, characterized in that the thickness of the actively electrochromic layer (16) is 250 to 500 nm.

46. Pane arrangement in accordance with claim 45, characterized in that the thickness of the actively electrochromic layer (16) is approximately 350 nm.

47. Pane arrangement in accordance with one of the preceding claims, characterized in that the second electrode layer (18) bears on its side facing towards the ion conducting layer (22) a passively or actively electrochromic charge storage layer (20).

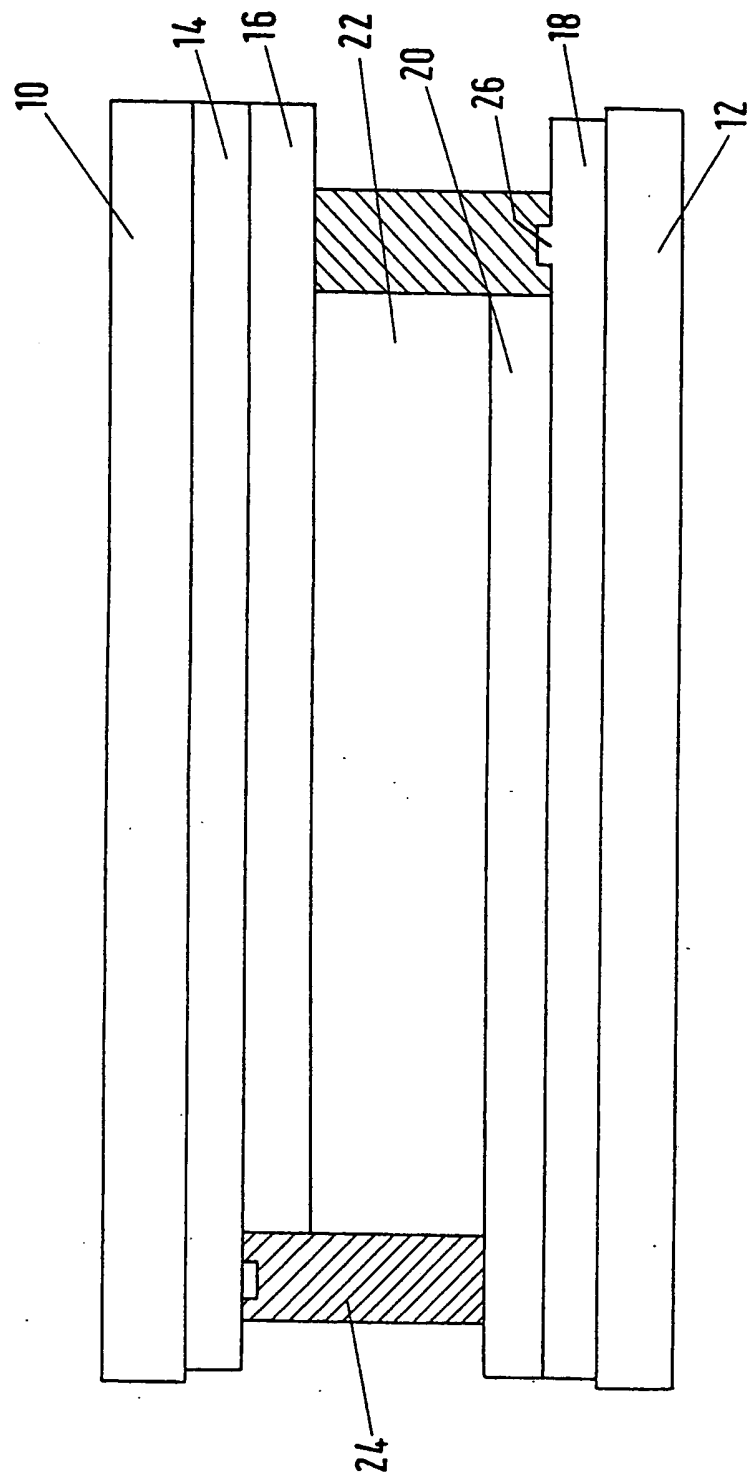
48. Pane arrangement in accordance with claim 47, characterized in that the charge storage layer (20) has a thickness of 200 up to 400 nm.

49. Pane arrangement in accordance with claim 48, characterized in that the charge storage layer (20) has a thickness of 280 nm.

50. Pane arrangement in accordance with one of claims 47 to 49, characterized in that the charge storage layer (20) consists of cerium titanium oxide, nickel oxide, cobalt oxide, chromium oxide, vanadium oxide and/or iridium oxide.

1/1

Fig.1



INTERNATIONAL SEARCH REPORT

Internat. Application No
PCT/EP 95/01861

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 G02F1/15		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 G02F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP-A-0 265 830 (HITACHI MAXELL LTD.) 4 May 1988 see page 2, line 50 - page 5, line 15 ---	1,2,4,6, 43
X	EP-A-0 434 359 (IMPERIAL CHEMICAL INDUSTRIES PLC) 26 June 1991 see page 3, line 18 - line 48 see page 6, line 1 - line 33 see page 8, line 2 - line 5 see page 8, line 57 - page 9, line 12 see page 9, line 46 - line 52 ---	1,4,6, 19,41, 43,45
X	EP,A,0 545 041 (CORNING INCORPORATED) 9 June 1993 see page 2, line 50 - page 4, line 6 --- <div style="text-align: right;">-/--</div>	1,2,4,6, 43
<div style="display: flex; justify-content: space-between;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex. </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center;">17 August 1995</div>		Date of mailing of the international search report <div style="text-align: center;">20.09.95</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016		Authorized officer <div style="text-align: center;">Volmer, W</div>

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/EP 95/01861

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	PATENT ABSTRACTS OF JAPAN vol. 8 no. 72 (P-265) ,4 April 1984 & JP,A,58 216225 (MATSUSHITA DENKI SANGYO KK) 15 December 1983, see abstract -----	1,2,6

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